

Ferrite synthesis in microstructured media: Template effects and magnetic properties

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Inverse micelles and organogels provide novel environments to synthesize ferrite particles. The fluid microstructure provides a template for the synthesis. Our experiments with ferrite synthesis in inverse micelles indicate the formation of superparamagnetic nanoparticles. Of interest is the encapsulation of these particles in polymer microspheres. The encapsulation is done using simple polymer precipitation in the micellar nonsolvent. The process results in a polymer-ferrite composite exhibiting supermagnetism. Low temperature spin glass properties of the composite are characterized through SQUID measurements. These composites have a superparamagnetic blocking temperature of 16 K and follow Curie–Weiss law at temperatures above 60 K with the fitted parameters: $C = 0.941$ emu/g K, $\theta = -287$ K, and $TIP = 0.0001$ emu/g. Since the polymer used is polyphenol, a highly functionalizable material, the composite is well suited for applications in magnetic bioseparations and magnetic coatings. © 1997 American Institute of Physics. [S0021-8979(97)59408-4]

I. INTRODUCTION

Due to the novel properties exhibited by particles of very small dimensions, there has been growing interest in the synthesis of nanoscale inorganic materials. Many researchers have successfully synthesized fine particles exploiting the restricted environments offered by surfactant systems. Water-in-oil (w/o) microemulsions (also known as reversed micelles),¹ liquid crystals,² and vesicles³ are examples of such systems used in nanoparticle synthesis.

We have recently found that it is possible to dissolve a presynthesized polymer [poly(4-ethylphenol)] in an appropriate solvent, and to reprecipitate it in spherical morphology, using water-in-oil microemulsions (also known as reverse micelles) as a nonsolvent medium. While a number of generic methods exists for fabricating microspheres,^{4–6} precipitation using water-in-oil microemulsions is a new technique and has some unique features. One of these, described here, is the fact that intramicellar solutes (e.g., nanoclusters solubilized within reverse micelles) become trapped in the precipitating polymer matrix. Thus, in addition to microsphere formation, such precipitation can be used as a microencapsulation method. Here we describe synthesis of nanophase ferrite particles, the microencapsulation of these particles in polymer microspheres, and the magnetic characterization of the resulting superparamagnetic inorganic–organic composite material. The inorganic component is iron oxide and the organic component is the polymer poly(*p*-ethylphenol).⁷

II. EXPERIMENT

A. Synthesis of ferrite particles

Stock solutions of 0.5 M AOT [bis(2-ethylhexyl) sodium sulfosuccinate] were used in preparing the reversed micellar

solutions containing the reactants FeSO_4 and NH_4OH . The so-called injection method was used in preparing all reversed micellar solutions. In a typical preparation, a predetermined amount of reactant stock solution was added to the AOT solution to yield the final reversed micellar solution with the required w/o ($[\text{H}_2\text{O}:\text{AOT}]$ (molar ratio of water to surfactant) and reactant concentration. The synthesis of ferrite particles was initiated by adding the NH_4OH reversed micellar solution to the FeSO_4 reversed micellar solution, while vigorously stirring the mixture. The solution instantly turned bluish green and within minutes changed to a deep red color. The reaction mixture was continuously stirred for about 2 h.

B. Synthesis of poly(4-ethylphenol) particles

The specific polymer used here is poly(4-ethylphenol) (PEP), which is synthesized using an oxidative enzyme, horseradish peroxidase, in the microstructured media of water-in-oil microemulsion.^{8,9} The polymer formed is recovered, washed several times with isooctane to remove the traces of adsorbed surfactant, dried, and stored for future use.

C. Synthesis of the ferrite-PEP composite

The presynthesized polymer was taken and redissolved in acetone (0.1 g polymer/ml acetone)(solution A). A second solution (nonsolvent solution B) consisting of the reverse micellar solution at an AOT concentration of 0.5 M and the required w_0 (w_0 is the water to surfactant molar ratio) was also prepared and contained the $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles (which were to be entrapped within the precipitated polymer microspheres) as an intramicellar solute. Typically, in all experiments, 1 ml of solution A was added to 20 ml of solution B in small aliquots with stirring. The clear solution B becomes cloudy immediately after the addition of a drop of

solution A, indicating that the dissolved polymer has phase separated. After the addition is completed, the mixture is kept being stirred briefly. The supernatant is then removed, and the polymer phase washed thoroughly with isooctane to remove traces of surfactant. Similar microsphere particles isolated from direct polymer synthesis are illustrated in a previous publication.⁷

D. Magnetic measurements

The magnetic properties of the ferrite-PEP composites were characterized using a Quantum Design, Inc. model MPMS-5S superconducting quantum interference device (SQUID) susceptometer. Calibration and measurement procedures were reported elsewhere.¹⁰ Several experiments were conducted: magnetic susceptibility (χ_{dc} , M/H) as a function of temperature and magnetization as a function of field or temperature. Two different procedures were used for the dc magnetic susceptibility experiments: (i) zero-field cooling, where the sample was slowly cooled in zero field to a temperature of 17 K at which the measuring field of 1.0 kG was switched on and the magnetization was measured as a function of temperature, and (ii) field cooling where the field of 1.0 kG was turned on at a temperature well above the superparamagnetic blocking temperature before the sample was cooled to 1.7 K.

For remanent magnetization measurement, both thermal remanent magnetization (TRM) and isothermal remanent magnetization (IRM) were obtained as a function of field. The TRM experiment involves slowly cooling the sample in an applied magnetic field to a measuring temperature below the blocking temperature and then switching off the field and measuring the remanent magnetization after a specified elapsed time of 300 s. On the other hand, IRM data are obtained by cooling the sample to the measurement temperature in zero field, applying a field for a specific time (300 s), and then switching off the field and measuring the remanent magnetization after an elapsed time of 300 s. Standard M vs H hysteresis loops were also recorded at different temperatures ranging from 2.0 to 300.0 K.

III. RESULTS AND DISCUSSION

Reversed micelles are nanodroplets of water sustained in an organic phase by a surfactant, typically an anionic *bis*(2-ethylhexyl) sodium sulfosuccinate, also referred to as AOT. The water pools of the micelles are capable of solubilizing biomolecules such as enzymes, which retain catalytic activity in what is essentially a minimal water environment.

A remarkable aspect of polymerization in this media is that the polymer formed precipitates out from solution with the morphology of interconnected, submicron-sized spheres. While the full explanation of morphology development is as yet unclear, the micelles have a templating effect on presynthesized polymers, they fold chains to the resulting spheres. As a consequence of the observation of polymer precipitation in the form of interconnected spheres, the concept of preparing polymer-nanoparticle composites arose from the argument that the precipitating polymer may also entrap and pull down inorganic clusters present in the micelles.

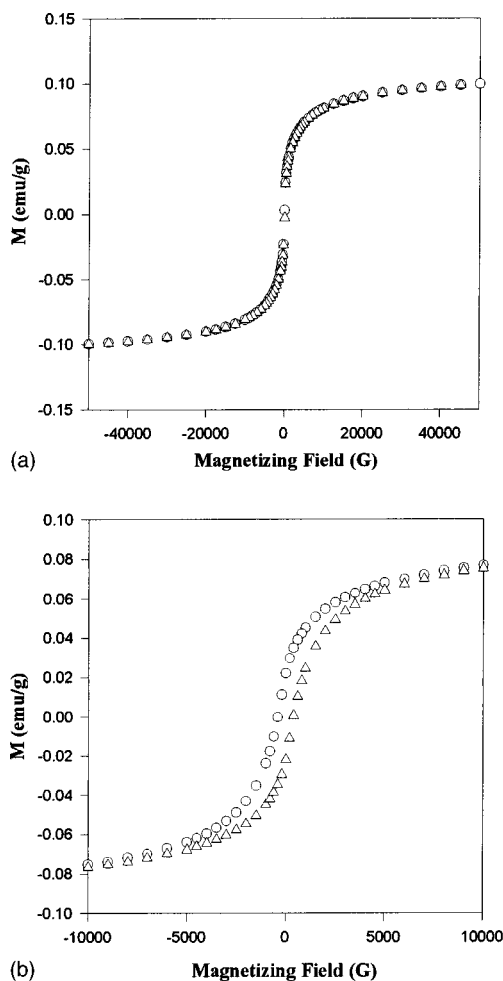


FIG. 1. (a) Magnetic hysteresis loop for ferrite polymer composite at 100 K and (b) magnetic hysteresis loop at 4.5 K.

Polymer-nanoparticle composites are prepared by a two step approach. In the first step, the water pools of the micelles are used to synthesize inorganic compounds whose growth would be restricted to the nanometer size range by the microstructure synthesis environment. In the second step, presynthesized polymers were added to reverse micellar solutions resulting in precipitation of microsphere composites.

Reversed micelles constitute a microreactor environment to synthesize inorganic particles restricted to the nanometer size range. As shown by Lopez-Quintela and Rivas,¹² ferrite particles synthesized in reversed micelles have sizes approaching the magnetic domain size. Such particles exhibit superparamagnetic properties. Here we show that incorporation of these ferrite particles into the polymer microspheres confers superparamagnetic properties to the composite.

A. Magnetic properties

Field-dependent hysteresis loops were generated in the temperature range 2.0–300 K. Typical trends exhibited by the ferrite-PEP composites are described through the hysteresis loops recorded at 100 and 4.5 K shown in Figs. 1(a) and 1(b), respectively. The magnetization versus field data at 100 K illustrate that the data are perfectly superimposable as the field is cycled between ± 50 kG, with the coercivity $H=0$.

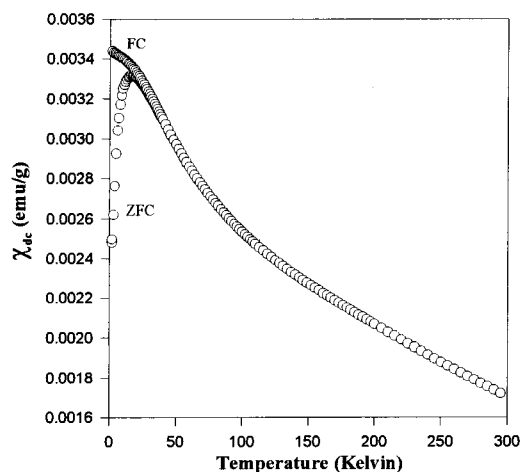


FIG. 2. Field-cooled (FC) and zero-field-cooled (ZFC) dc magnetic susceptibility data for the ferrite polymer composite plotted over the 1.7–300 K temperature region.

This lack of hysteresis is characteristic of superparamagnetic particles or single-domain particles of very small dimensions.

As the temperature is significantly lowered to 4.5 K, the sample starts to display some hysteresis with coercivity $H=500$ G, as seen in Fig. 1(b). The presence of low-temperature hysteresis together with the absence of hysteresis at higher temperature confirms the superparamagnetism of the ferrite-PEP composite. If the sample did not show hysteresis at any temperature, it would be classified as being made of single-domain particles with the hard axis aligned.¹³

Temperature-dependent dc magnetic susceptibility data for the sample obtained by two different methods are shown in Fig. 2. At high temperatures, the field-cooled (FC) and zero-field-cooled (ZFC) magnetization data exhibit the same trend. However, at low temperatures they significantly diverge. The FC curve reaches a plateau and the ZFC curve shows a dramatic decrease in magnetization. From the ZFC data in Fig. 2, it is apparent that there is a sharp maximum in the magnetization when plotted as a function of temperature. This maximum is a characteristic of spin glass type materials¹⁴ and, for the ferrite-PEP composite studied here, it occurs at 16.0 K. Magnetic particles of very small size are known to mimic some of the properties of spin glass materials and to exhibit blocking temperatures.^{14,15} Going back to the hysteresis loops shown in Fig. 1, it is worth noting that the sample exhibits hysteresis at temperatures below 16.0 K with hysteresis vanishing at higher temperatures. The observation is consistent with the behavior of ultrafine magnetic particles.¹⁵ The dc magnetic susceptibility data were fit to the Curie–Weiss law at temperatures above 60 K. This temperature region is in the superparamagnetic domain and the fitted parameters are $C=0.941$ emu/g K, $\theta=-287$ K, and $TIP=0.0001$ emu/g.

One of the frequently performed diagnostic experiments to characterize the spin glass state is measuring the depen-

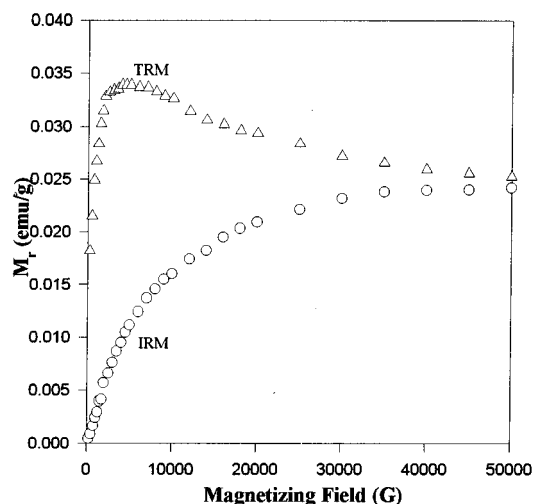


FIG. 3. Isothermal remanent magnetization and thermal remanent magnetization data for the ferrite polymer composite plotted as a function of remanent inducing magnetic field.

dence of TRM and IRM on the applied magnetic field. The TRM and IRM data as a function of field at 4.5 K are shown in Fig. 3. The TRM attains a maximum at 3.5 kG and then slowly decreases and remains essentially invariant above 20 kG. The IRM increases sharply until about 20 kG and eventually reaches a plateau at magnetic fields above 35 kG.

ACKNOWLEDGMENTS

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